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Localized Corrosion Susceptibility of Alloy 22 in Na-K-Cl-NO₃ Brines at 110 to 150°C

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Abstract – Electrochemical cyclic potentiodynamic polarization experiments were conducted to assess crevice corrosion of Alloy 22 in de-aerated aqueous solutions of chloride and nitrate salts of potassium and sodium in the temperature range 110-150°C. The tests were run in neutral and slightly acidic aqueous solutions. The Alloy 22 specimens were multiple creviced weld prisms. No evidence of crevice corrosion was observed in the range 125-150°C.

In the 120 to 160°C temperature range, the anionic concentration of stable aqueous solutions is dominated by nitrate relative to chloride. At nominally 120°C, the minimum nitrate to chloride ratio is about 4.5, and it increases to about 22 at nominally 155°C. The absence of localized corrosion susceptibility in these solutions is attributed to the known inhibiting effect of the nitrate anion.

Aqueous solution chemistry studies indicate that nitrate to chloride ratios of less than 0.5 are possible for temperatures up to nominally 116°C. At 110°C, aqueous solutions can have dissolved chloride well in excess of nitrate. Localized corrosion was observed at nitrate to chloride ratios up to 1.0, the highest ratio tested. The extent of localized corrosion was confined to the crevice region of the samples, and was limited for nitrate to chloride ratios greater than or equal to 0.3.

I. INTRODUCTION

Alloy 22 (a nickel-chromium-molybdenum-tungsten alloy) is being investigated for use as the outer barrier of waste containers for a high-level nuclear waste repository in the thick unsaturated zone at Yucca Mountain, Nevada. In this non-pressurized environment, aqueous solutions may form and stably exist above the nominal boiling point of water due to high salt content [1, 2]. The majority of the aqueous solutions that are predicted to form on the waste packages due to dust deliquescence consists of chloride and nitrate salts of sodium and potassium [1, 2]. Recent work indicates that deliquescence of these salt mixtures can occur at temperatures in excess of 180°C [3]. Hence, understanding the degradation of Alloy 22 in these environments is necessary for the long-term prediction of waste package integrity.

Previous corrosion studies have shown that nitrate is an effective inhibitor of localized corrosion of corrosion resistant metal alloys [4, 5]. This has been demonstrated for Alloy 22 in the temperature range 60 to 100°C for aqueous solutions of 1, 3.5 and 6 molal Cl [5]. In this study, localized corrosion inhibition was observed at 60°C with nitrate to chloride ratio of 0.15 and at 100°C with a ratio of 0.5.

Aqueous solution composition dependence on relative humidity (RH) for the NaCl + KNO₃ system has been studied by at 90 and 120°C [6]. At 90°C chloride-only (i.e., no nitrate) solutions are possible, however at 120°C stable chloride solutions must also contain nitrate. The minimum nitrate to chloride ratio occurs at the maximum RH (which depends on the temperature and the total pressure). This ratio at 120°C is approximately 3, with NO₃ and Cl concentrations at 19 and 6 molal, respectively.

More recently the aqueous solution composition dependence on RH for the NaCl + KNO₃ + NaNO₃ aqueous salt mixture at 120°C has been investigated [7]. For this system, the minimum nitrate to chloride ratio occurs at a measured RH of nominally 50% and is approximately equal to 5 with NO₃ and Cl concentrations at 25 and 5 molal, respectively.

II. EXPERIMENTAL

Stable aqueous solution compositions of NaCl, KCl, NaNO₃, and KNO₃ mixtures were evaluated over the temperature range 110 to 160°C. For temperatures greater than 120°C, chloride solubility limits in fixed nitrate concentration solutions were determined. For

temperatures less than 120°C, nitrate solubility limits in fixed chloride concentration solutions were determined. Boiling points were determined for all solutions.

Equi-molar mixtures of $\text{KNO}_3 + \text{NaNO}_3$ and $\text{NaCl} + \text{KCl}$ were used as starting solutions because literature indicates that maximum chloride solubility occurs when sodium and potassium are present in nearly equal molar concentrations [8]. Salt additions to determine solubility limits were made with alternating additions of the Na and K salts.

Localized corrosion susceptibility of Alloy 22 was evaluated using the electrochemical cyclic potentiodynamic polarization (CPP) technique [9]. The Alloy 22 specimens were weld prism specimens. Crevices were formed with ceramic crevice formers with a polytetrafluoroethylene (PTFE) sheet between the crevice former and the metal surface. Crevice formers were tightened to 70 inch-lb. De-aeration was performed with nitrogen gas. Electrochemical tests were run in solutions with and without acid addition. When acid was added it was to a concentration of 10^{-4} molal.

Localized corrosion susceptibility was evaluated from analysis of the CPP curves and post-test examination of the specimen surfaces. From the CPP curves, the potential on the reverse scan of the curve where the current density is equal to 1×10^{-6} amps/cm² was determined. This potential is designated ER1 and is an indicator of a materials ability to repassivate after undergoing degradation. The post-test surface examination was performed with optical microscopy in order to evaluate the extent the degradation of the Alloy 22 specimen that occurred during the CPP tests.

III. RESULTS AND DISCUSSION

III.A. Aqueous Solution Chemistry

The boiling point temperature dependence on solution compositions for various mixtures of nitrate and chloride is shown in Figure 1. The data for nitrate compositions greater than 20 molal was obtained by adding chloride to fixed nitrate solutions until the solubility limit was reached. The data for nitrate compositions of less than 20 molal was obtained by starting with a fixed chloride molality and then adding nitrate until the solubility limit was reached.

The data shows that in the 120 to 160°C temperature range, the anionic concentration of stable aqueous solutions is dominated by nitrate over chloride ($\text{NO}_3 / \text{Cl} > 1$). At nominally 120°C the minimum nitrate to chloride ratio is about 4.5, and at nominally 155°C it increases to about 22. At temperatures less than about 116°C the minimum nitrate to chloride ratio could be less than 1, hence chloride dominated solutions are possible. Figure 2 graphically illustrates the temperature dependence of the

minimum nitrate to chloride ratio as a function of temperature.

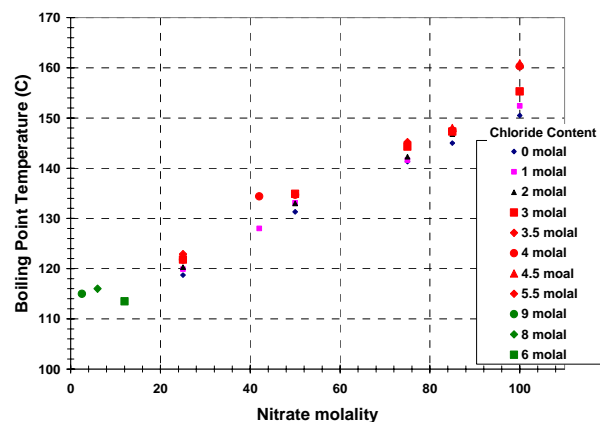


Figure 1. Boiling point temperature dependence on solution composition. See text for details.

These studies indicate that deliquescence of salts (dust) could produce aqueous solutions with nitrate to chloride ratios of less than 1 for temperatures up to at least 116°C. However, the exact upper temperature limit for the transition from chloride dominated to nitrate dominated has not been determined, but it appears to be in the range 117 to 120°C.

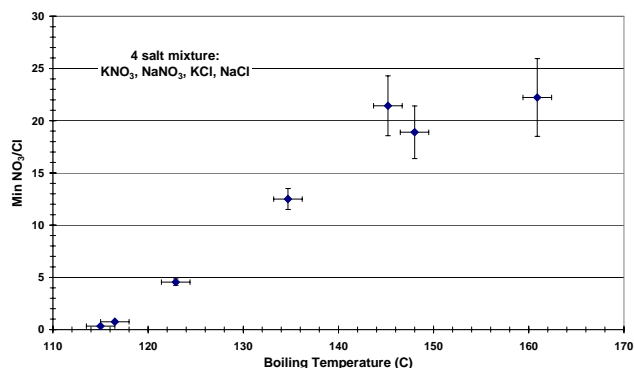


Figure 2. Minimum nitrate to chloride ratios for four-salt (KNO_3 , NaNO_3 , KCl , NaCl) solutions with boiling temperatures above 115°C.

Minimum NO_3 to Cl ratios derived from solubility data from deliquescence testing agree well with the data in Figure 2. From data on a salt mixture of $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3$ at 120°C the measured solubility data give a minimum NO_3 to Cl ratio that is about 5 [7]. And from data on a salt mixture of $\text{NaCl} + \text{KNO}_3$ at 120°C the measured solubility data give a minimum NO_3 to Cl ratio that is about 3 [6]. From Figure 2, the interpolated minimum nitrate to chloride ratio is approximately 3.

III.A. Electrochemical Corrosion Studies

The localized corrosion susceptibility of Alloy 22 in the high temperature Na-K-NO₃-Cl aqueous solutions, was assessed using electrochemical cyclic potentiodynamic polarization testing.

The repassivation potential, ER1, as a function of the nitrate to chloride ratio is plotted in Figure 3. The plot includes data from testing in solutions from 110 to 150°C. The data points in the figure also indicate whether optical microscopy evaluation indicated localized corrosion. The data show a steady increase in ER1 with increasing nitrate to chloride ratio up to about a value of 1 and then a nearly constant value of ER1. The occurrence of localized corrosion was observed for nitrate to chloride ratio up to 1, however localized corrosion was minimal for ratios greater than 0.3.

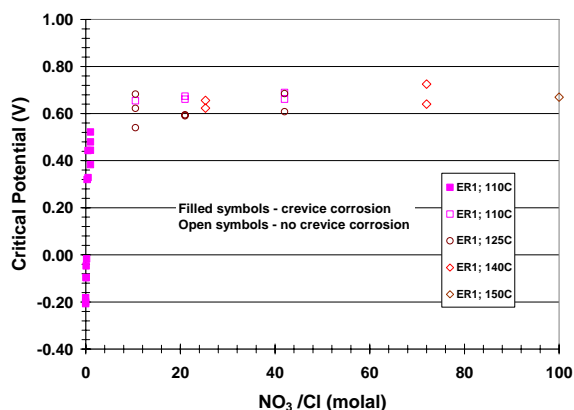


Figure 3. ER1 as a function of nitrate to chloride ratio in aqueous solutions of NaCl, KCl, NaNO₃, and KNO₃ and in the temperature range 110 to 150°C.

Crevice corrosion of Alloy 22 was not observed in aqueous solution mixtures of NaCl, KCl, NaNO₃, and KNO₃ at 125, 140, and 150°C. Chloride concentrations ranged from 1 to 4 molal, and nitrate concentration ranged from 42 to 100 molal. The minimum nitrate to chloride ratios in the test solutions are 10.5, 25.3, and 100 at 125, 140, and 150°C, respectively.

Crevice corrosion of Alloy 22 was observed at 110°C using CPP. At nitrate to chloride ratios greater than 0.3, the observed crevice corrosion was very limited. At lower ratios, there was significant crevice corrosion observed. Chloride concentrations ranged from 1 to 8 molal, and nitrate concentration ranged from 0.8 to 42 molal at 110°C.

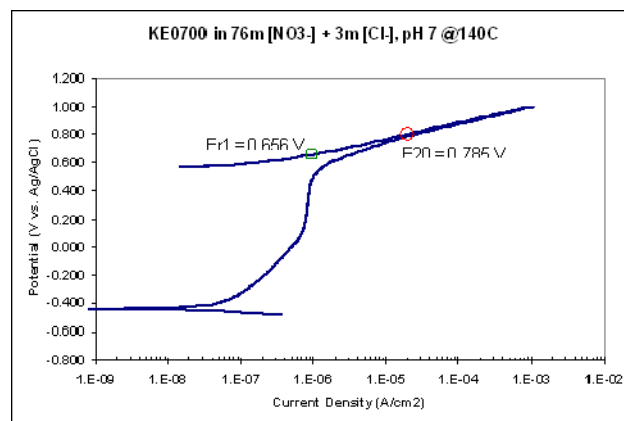


Figure 4. CPP curve for test where optical examination showed no localized corrosion.

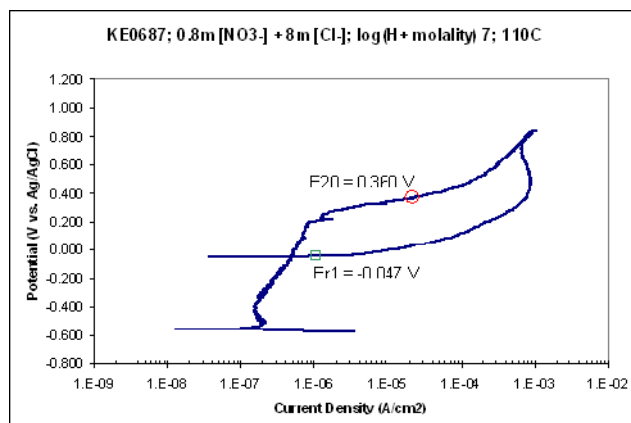


Figure 5. CPP curve for test where optical examination showed localized corrosion.

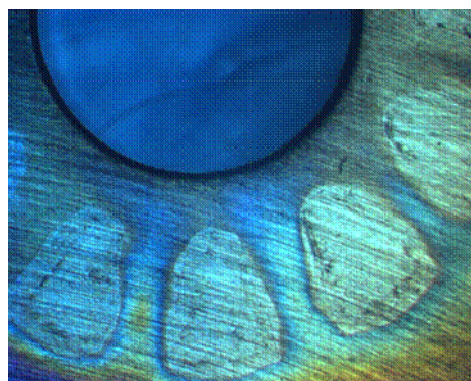


Figure 6. After CPP test in 8m [Cl-] + 4m [NO₃-] solution, [NO₃-]/[Cl-] of 0.5:1, and 110°C. Limited crevice corrosion observed.

The inhibition of Alloy 22 localized corrosion by nitrate is consistent with previous studies for sodium + potassium based chloride and nitrate solutions. Those tests showed that nitrate inhibition of localized corrosion of Alloy 22 in the temperature range 60 to 100°C increases with increasing nitrate to chloride ratio. The present study shows that slightly higher ratios are necessary for inhibition at 110°C. At temperatures greater than nominally 120°C, the stable solutions have nitrate well in excess of chloride and inhibition of localized corrosion occurs.

II. CONCLUSIONS

Localized corrosion susceptibility of Alloy 22 was evaluated using electrochemical CPP technique in stable aqueous solution from 110 to 150°C. Nitrate is an effective inhibitor of Alloy 22 localized corrosion at elevated temperatures. No localized corrosion was observed for $T > 125^{\circ}\text{C}$ and this is attributed to stable solutions requiring nitrate well in excess of chloride. Localized corrosion was observed at 110°C, however the extent was limited for nitrate to chloride ratios greater than 0.3.

Supporting studies of the stability of Na-K-NO₃-Cl aqueous solutions were also performed. Under atmospheric conditions, stable aqueous solutions of mixtures of NaCl, KCl, NaNO₃, and KNO₃ are dominated by nitrate ($\text{NO}_3 / \text{Cl} > 1$) for temperatures greater than 120°C. For temperatures less than 116°C, the solutions could be dominated by chloride over nitrate ($\text{NO}_3 / \text{Cl} < 1$).

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